Research and Development of the pyrochemical processing for the mixed nitride uranium-plutonium fuel

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Research and Development of the pyrochemical processing for the mixed nitride uranium-plutonium fuel

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Abstract. A mixed nitride U-Pu SNF pyrochemical reprocessing technology was suggested. It includes the following basic operations: dissolution of key components using the CdCl2 or PbCl2 oxidizer in chloride melt and their subsequent deposition as oxides. The obtained product, which is a mixture of actinides and rare-earth metals, may be additionally purified using hydrometallurgical processes (combined technology) or using pyrochemical methods. The mixture of actinides oxides is reduced to metal ("metallization"), additionally purified from fission products during electrorefining and then Am and Cm are separated using the potentiostatic electrolysis in order to obtain products that may be used for pure fuel fabrication.

1. Introduction

One of the primary benefits of the pyrochemical processes application for the technology of the spent nuclear fuel (SNF) on fast neutron reactors (FNR) processing at the closure of the nuclear fuel cycle (NFC) is the possibility of reducing the SNF exposure time to 1 year, since the molten salts are the radiation-resistant media and can be used in the SNF processing with a high energy release. A technological scheme for the mixed nitride uranium-plutonium (MNUP) SNF processing was proposed. This scheme includes the following basic operations: dissolution of the target components using an oxidizing agent (CdCl2 or PbCl2) in the chloride melt with the subsequent deposition them as oxides. The derived product is a mixture of actinides and rare-earth metals (REM) oxides, which can be sent for further purification using hydrometallurgy (combined technology) or processed by means of the pyrochemical methods.

In order to obtain the product appropriate for the pure fuel production, the mixture of the actinide oxides is reduced to the metal ("metallization"), additionally purified from the fission products (FP) by electrorefining; and then the Am and Cm are separated with the use of the potentiostatic electrolysis.

The results of the Research and Development (R & D) related to the experimental and theoretical substantiation of the main procedures of the proposed technological schemes for the pyrochemical processing of the MNUP SNF FNR, obtained in 2016-2017, are presented in this work.

2. The R&D objectives and tasks

The main objective of the R & D is the creation of a pyrochemical process as a part of a combined (PYRO + HYDRO) technology for the processing the MNUP SNF at the reprocessing module of the pilot demonstration energy complex (RM PDEC). The goal of the pyrochemical processing as a part of the combined technology is to extract the target processing products (U-Pu-Np-Am) and purify them from the fission products (FP) to a level that meets the requirements of the hydrometallurgical processing.

According to the combined scheme, the products of the pyrochemical processing, purified from the main mass of the FP with a content of 99.9% of fission materials (FM) (the loss of the FM in radioactive wastes (RW) is not more than 0.1%, in general), should be supplied to the hydrometallurgical processing stage. During the hydrometallurgical stage, the products of the pyrochemical processing are post-refined from the FP to the level that allow producing the nitride NF by the same technology and in the same protective and technological equipment as for the manufacture of the initial reactor loading.

Development of a strictly pyrochemical technology for the processing of the MNUP SNF for use in the industrial energy complex (IEC), including the extraction of the target components (U-Pu-Np-Am) and their purification from the FP to the level that meets the requirements of the nuclear fuel regeneration.

3. Technological charts of the MNUP SNF FNR pyrochemical processing

3.1. Combined (PYRO+HYDRO) technology

The principal procedure in the technological chart of the MNUP SNF combined processing is a “soft” chlorination, intended to transfer the entire mass of the FM into the melt in the form of chlorides using an oxidant, that is the lead chloride (the cadmium chloride).

The volatile fission products, nitrogen, noble metals (NM), Mo, Tc, and Zr are removed at this stage of the process flow. In case of the combined chart implementation for the reprocessing of the SNF on RM PDEC, the melt containing the FM and a number of FP (alkali-earth (AE), rare earth metals (REM), rare earth elements (REE)) directs to the next operation of the actinide oxides deposition (oxide titration).

For this purpose, the lithium oxide is supplied to the melt. The formed An oxides with the REE oxides admixture are filtered and directed to the hydrometallurgical process stage for the purification from the FP with the subsequent transfer to the fabrication of fuel, and the filtrate (the chloride electrolyte) is sent to the regeneration for the purification from alkali and alkali earth metals.

The chart of the SNF processing for the RM PDEC in the combined version is presented in figure. 1. The proposed technological chart allows obtaining the NM in a form convenient for the hydrometallurgical redistribution (oxides) and reducing the activity to a level that allows using this product in the hydrometallurgical process stage of the combined scheme.

3.2. Strictly pyrochemical technology

In case of the implementation of the strictly pyrochemical technology for the SNF processing (for IEC) after the operation of the “soft” chlorination and the withdrawal of the part of the FP from the process flow, as described in section 1.1, the melt containing the total mass of NM is delivered to the oxide precipitation operation. At this stage, up to 70% of the uranium being in the melt is precipitated as oxides.

After filtration the uranium oxide precipitate is washed out by the pure molten electrolyte and is removed from the process flow; and the melt containing the NM, REE, and the uranium residues is proceeded to the An post - precipitation. The obtained precipitate of the actinide oxides, containing from 5 to 10% of the REE oxides, is filtered out and sent to the electrochemical reduction procedure (“metallization”). After the reduction of the oxides, the metal fraction is remelted and directed to the electrochemical refining, in which a solid soluble anode and a solid cathode are used. The obtained cathode product is subjected to the purification from the electrolyte and forwarded to refabrication.

The technological chart of the strictly pyrochemical processing of the SNF is presented in figure 2. The proposed chart makes it possible to drastically reduce the material flows of the technological media at the initial stage of processing (oxide precipitation procedure) and to simplify the instrumentation of the subsequent procedures.

4. Theoretical and experimental justification of the main technological procedures

4.1. Soft” chlorination

The basis of the technological procedure is the process of the chemical interaction of the oxidizing agent $PbCl_2$ ($CdCl_2$) with the components of the nitride fuel according to the reaction:

$$2Me + 3PbCl_2 \rightarrow 2MeCl_3 + 3Pb^0 \quad (1)$$

Where Me are the actinides and REE in the form of a metal. The process of the "soft" chlorination of the uranium mononitride (UN) with the cadmium chloride in the molten eutectic LiCl-KCl was investigated in dependence on temperature and content of the chlorinating reagent in the melt [1-5]. It was revealed that the conversion degree for $UN \rightarrow UCl_3$ increases almost linearly with the temperature rise and for the molar ratio $CdCl_2$ / UN = 2.6 is 23.5% at 500 °C and 100% at 750 °C.

The obtained results were confirmed by the large-scale laboratory experiments at the stand installations of JSC "SHK" (Tomsk) with a UN loading mass up to 170 g.

The $CdCl_2$ concentration equal to 50 wt% in the electrolyte was recommended. At low concentrations of the cadmium chloride the chlorination rate is significantly reduced and at high concentrations the conversion degree decreases and the amount of the salt sublimates increases.

The use of the lead chloride ($PbCl_2$) as a chlorinating agent is of great interest for the "soft" chlorination process. The noble FP do not interact with the lead chloride in the chlorination process and remain in the metal phase, and the metallic lead formed by the reaction (1), which is a collector for the noble FP, is removed from the process flow and directed to the disposal area (RW).

The thermodynamic data analysis indicates the possibility of reducing the temperature by 50-100 °C using $PbCl_2$ as a chlorinating agent while maintaining the parameters and characteristics of the "soft" chlorination process.

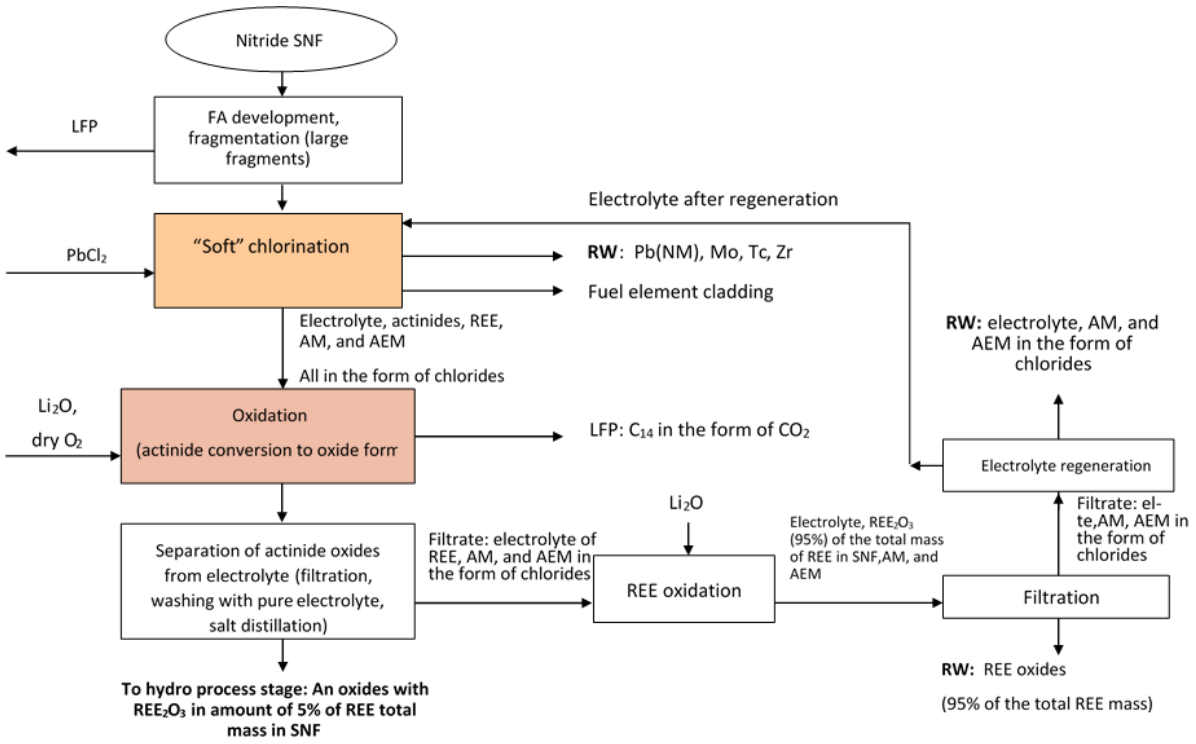

Figure 1. Technological chart of the combined (PYRO+COMBI) processing of the MNUP SNF FNR.

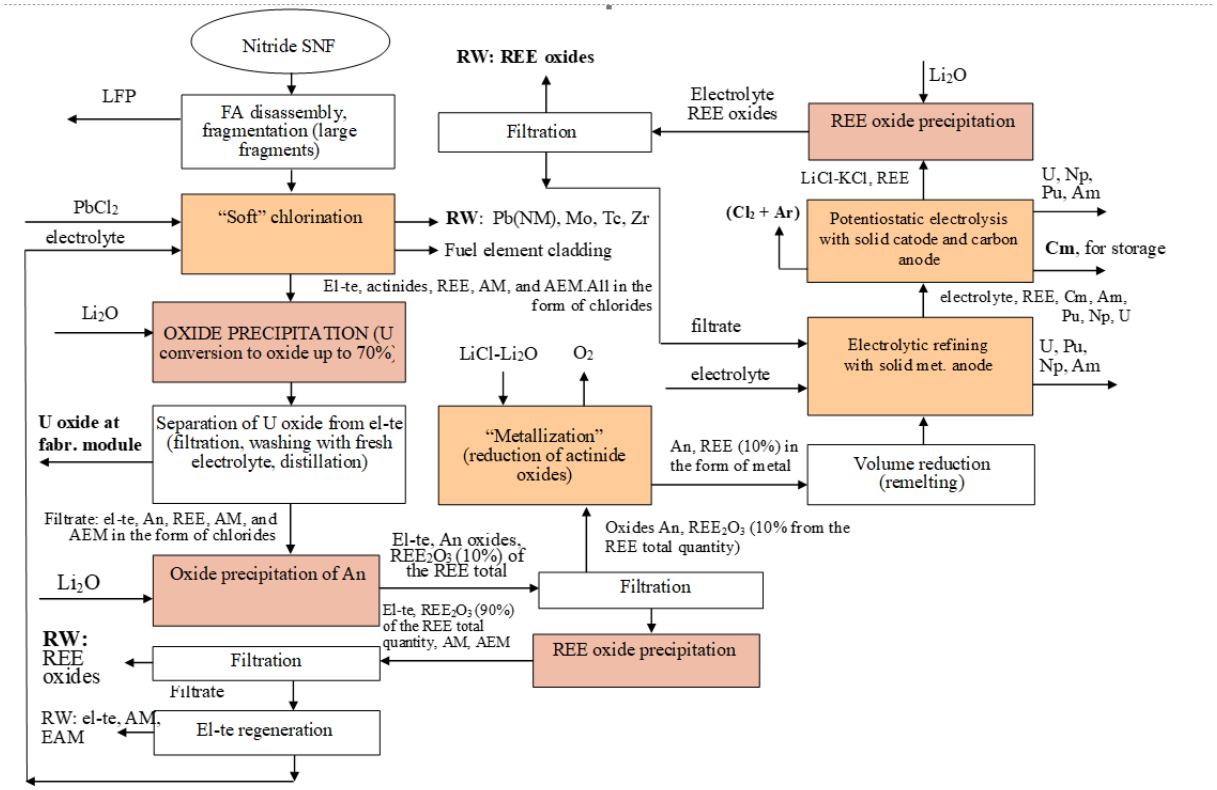

Figure 2. Technological chart of the strictly pyrochemical processing of the MNUP SNF FNR.

4.2. Reduction of the actinide oxides to metal ("Metallization")

The process of actinide oxides reduction was carried out using lithium, generated at the inert cathode during the electrolysis of the LiCl-Li_2O melt. The dissolved lithium interacts in the melt bulk with particles of the oxidized SNF, reducing the oxides of the fuel components contained in them, according to the scheme:

$$UO_{2+x} + (4 + 2x)Li_2^+ \rightarrow U + (2 + x)Li_2O + (4 + 2x)Li^+ \quad (2)$$

The formed lithium oxide dissolves in the LiCl melt [6], diffuses to the melt bulk and oxidizes at the graphite (consumable) anode with the release of the CO-CO_2 mixture:

$$2Li_2O + C - 4\bar{e} \rightarrow CO_2(CO)\uparrow + 4Li^+ \quad (3)$$

or at the inert (non-consumable) anode - with the oxygen gas evaluation:

$$2Li_2O - 4\bar{e} \rightarrow O_2\uparrow + 4Li^+ \quad (4)$$

When using the graphite anodes, the reduction product (metal powder of actinides) contained not only the metal phase, but also the actinide carbides. The process of the SNF oxides reduction to metal is realized with the use of the non-consumable (inert) anode.

The metals (Pt, Au, Ag), metal alloys (aluminum bronze, Cu-Fe-Ni), and oxide ceramics were investigated as inert anodes. Oxides were formed on the surface of platinum during the oxygen discharge, which led to the formation of the Li2PtO3 platinate, when interacting with the lithium oxide. The platinate is a poor electrical conductor, therefore, it peels off from the metal base with time that results in the anode destruction.

The Au and Ag anodes had a low corrosion resistance during electrolysis and intensively dissolved in the chloride melt. The oxide layer formed on the surface of the Cu – Fe – Ni alloys did not protect them from further oxidation and led to the intense corrosion. According to the research results, it was

established that the ceramic anodes based on NiO possess the highest corrosion resistance; they were further used for optimization of the "metallization" process.

During the experimental studies the technological parameters of the oxygen evolution process on the investigated ceramic anodes were determined. The limiting diffusion current density (ilim) of this process increases with the rise of the Li2O concentration and temperature and almost does not depend on the anode material. The following modes of electrolysis using ceramic anodes were identified for the metallization:

- LiCl melt with the Li2O content not less than 0.9-1.0 wt%;
- temperature: 650 °C;
- current density - not higher than 0.4 A/cm2 (potential - not higher than 3.0 V relatively to the lithium potential)

The reduction process of the UO2 powder and tablets (diameter - 5.0 mm, height - 8.0 mm) with a density of 97% of theoretical one was investigated in the laboratory electrolyzer. The possibility of a complete reduction of uranium dioxide to metal was revealed. It was established that the process of the UO2 reduction proceeds in the diffusion mode and is limited by the mass transfer in the pores of the tablet (particle) of the reduced uranium.

A technique for estimating the porosity of the metallized tablets was proposed. The amount of salt remaining in the pores of the metallized tablet was determined, which is 8% for chloride and 0.08% for lithium oxide of the total weight of the uranium metal.

The following modes of the "metallization" process for the uranium dioxide are recommended:

- - LiCl electrolyte with the addition of Li2O in an amount from 1.0 to 1.5 wt%;
- - process temperature: 650 ° C;
- - cathode potential 0.02 - 0.07 V (relatively to lithium potential).

Reduced UO2 tablets retain their original shape and geometric dimensions (figure 3).

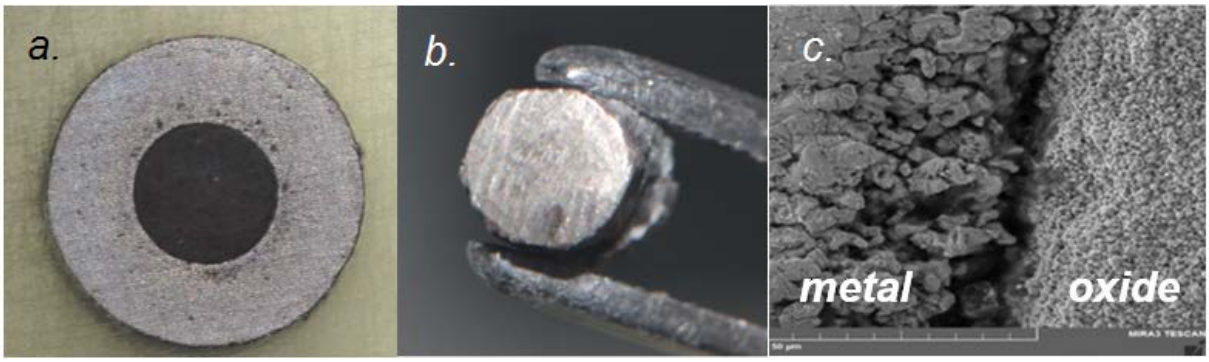

Figure 3. Images of UO2 tablets after the metallization procedure: partially and completely (a) reduced(b); micrograph of the reduction front of the tablet(c).

4.3. Electrolytic deposition of actinides in the chloride melt

The experimental study of the electrolytic deposition of uranium from the 3LiCl – 2KCl melt with the UCl3 addition were carried out; the cathode deposits of the uranium metal at the Mo cathode were obtained. A special attention was paid to the issue of the uniform current distribution over the surface of a solid cathode during the process.

The electrolysis process involved the preparation of a cylindrical anode made of the metallic uranium. For that purpose, the uranium was deposited by electrolysis on a molybdenum substrate, placed along the perimeter of the crucible, as shown in figure 4. Then, the uranium electrode on the Mo substrate served as a soluble anode, and the process of uranium deposition was performed at the Mo-cathode, which had a rod shape and was located in the center of the crucible.

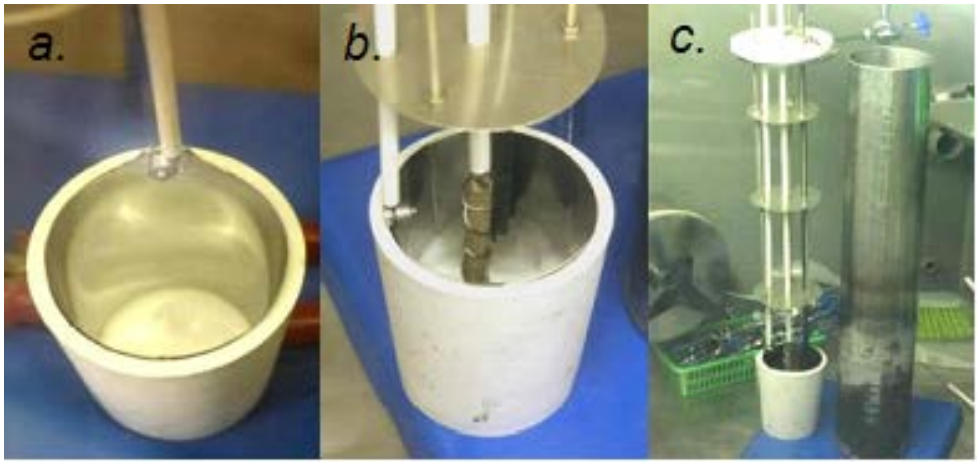

Figure 4. Images of the lab electrolyzer and its nods: crucible with Mo-counter electrode inside(a); crucible with electrode assembly(b); assembled electrolyzer(c)

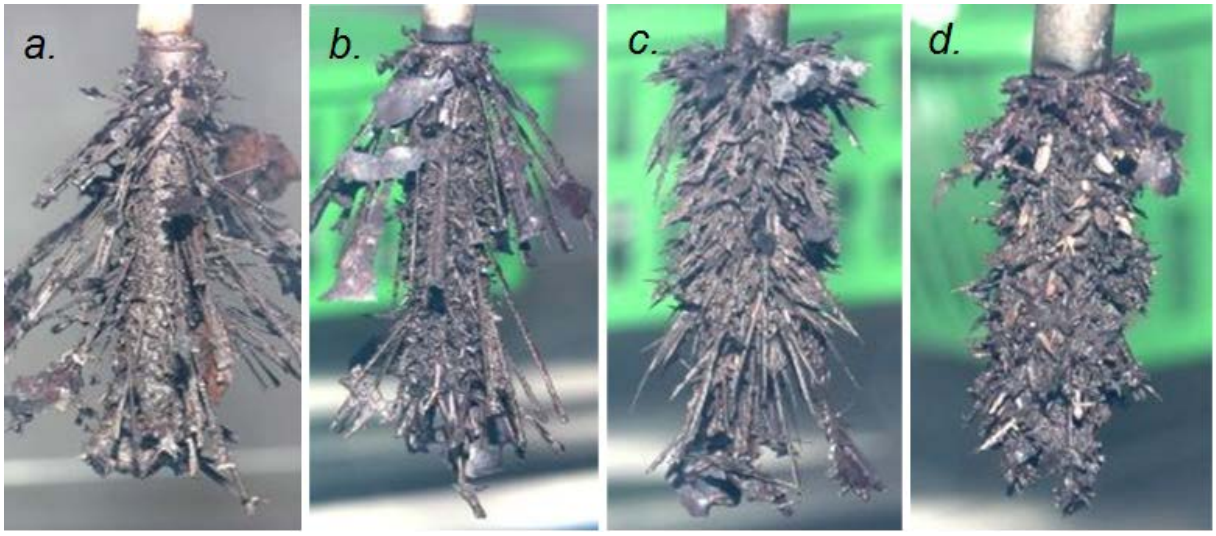

Figure 5. Images of uranium cathode deposits obtained at the Mo-cathode in the melt (LiCl-KCl) eut with the addition of UCl3 2.3 mol. % (12.7 wt %) at different temperatures, ° C: 500(a); b.550 (b); -600(c). Initial current density: 150 mA/cm2 with the exception of sample (d) (100 mA/cm2 at 600° C).

The morphology of the obtained cathode deposits depended on the concentration of uranium in the melt, temperature, and the cathode current density. At uranium trichloride concentration of 2.3 mol. % (12.7 wt%), the most compact deposit was obtained at the initial current density of 100-150 mA /cm2 and 600 ° C (figure 5). The obtained cathode deposits of uranium, purified from the electrolyte by the distillation method, are presented in figure 6.

4.4. Distillation of chloride electrolyte from pyrochemical processing products

Intermediate and final products of the SNF pyrochemical processing, that is the tablets or the metallized fuel powder as well as the actinides cathode deposit contain from 5 to 10 wt % of electrolyte mixed with the NM and the FP after electrolysis. The purification of these products from the electrolyte is necessary in order to remove or to reduce the concentration of the fission products (alkali and alkali earth chlorides) from the process flow as well as to decrease the losses of the target components contained in the melt in the form of chlorides.

One of the considered methods of purification from electrolyte is the distillation at elevated temperature and evacuation.

The experimental studies of the distillation process for the alkali and alkali earth chlorides from their molten mixtures under various conditions were carried out. It was indicated that the distillation process at temperature of 700-900 ° C and a residual pressure of 1 Pa allows removing 98.8-99.9 wt % of LiCl, KCl, and CsCl. At the same time, the uranium content in sublimates is negligible. The distillation process in these conditions reduces the NdCl3 concentration in the product remaining after the distillation by one order of magnitude, and BaCl2 and SrCl2 - by two orders of magnitude.

Tests related to the distillation of the molten LiCl – Li2O mixtures with a content of 3.0 wt % oxide verify that the lithium oxide, unlike chloride, is almost not distilled out. The modes of distillation were determined, which provide a decrease in the lithium concentration (as part of its chloride and oxide) in the metallized tablets and the uranium powders up to 0.01 wt %.

Following on from the conducted research, it can be concluded that the distillation method allows cleaning metallized products only from alkali chlorides. In order to remove the Li2O, impurities of chlorides or oxides of alkaline earth and rare earth elements, the other methods or techniques should be used that lead to the removal of the volatile components.

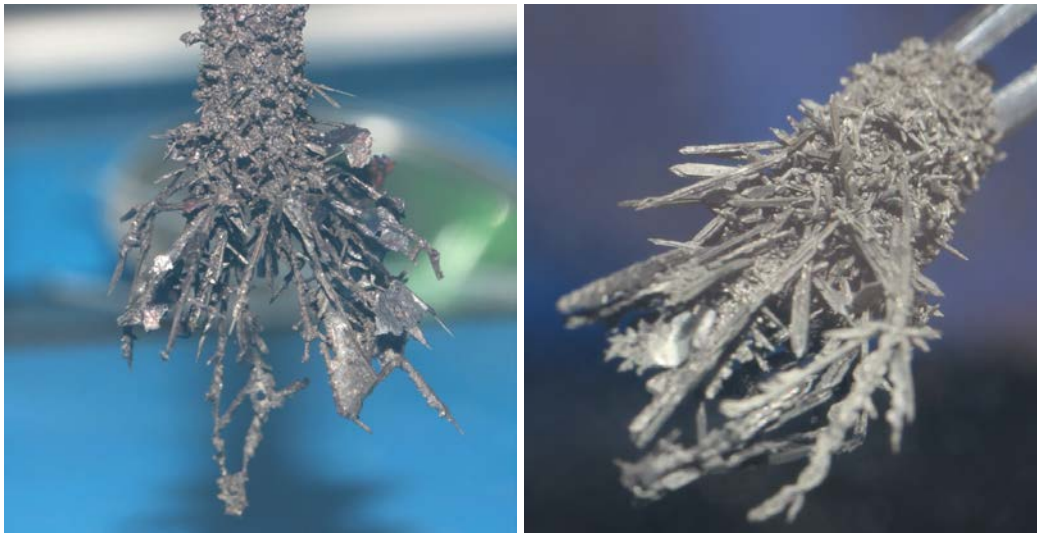

Figure 6. Images of the cathode deposit before (a) and after (a) the purification from the chloride electrolyte using the distillation technique.

4.5. Oxide deposition of actinides and chloride melts filtration

The optimization of the oxide deposition process for the REE was performed using the neodymium trichloride. The lithium oxide and oxygen gas were used as precipitants agents.

The thermodynamic calculations performed by means of the HSC Chemistry (6.1) revealed that the main product of the NdCl3 interaction with the lithium oxide in the LiCl- (KCl) melt with a molar ratio of Li2O: NdCl3 (less than one) is the neodymium oxychloride. As the amount of the lithium oxide increases, the amount of the formed neodymium oxychloride decreases, and the amount of the neodymium oxide rises. The results of the calculations were confirmed by the experimental data.

According to the tests results, it was also established that the particle size distribution of the obtained neodymium deposits weakly depended on temperature and the initial O2–: Nd3 + molar ratio in the studied range from 0.5 to 2.0. The maximum of the particle size distribution curves is in the range of 20–40 μm, although in some cases a significant fraction of the particles had sizes at the level of hundreds of microns. It should be noted that at least 50 wt % of the solid oxide phase consists of particles not exceeding 10 μm, and the content of particles with a size less than 1 μm is approximately 5% (figure 7).

The melt interaction with the gaseous oxygen is a complex heterogeneous process, the rate of which is determined by the value of the specific surface interface of the liquid (melt) and gaseous (oxygen) phases. The neodymium deposition degree from the chloride melt found in the experiments was 50% at using 50 mol O2 per 1 mol Nd (III), which corresponds to the O: Nd = 100 molar ratio.

The obtained theoretical and experimental data of the oxide deposition process of the REM allows us defining the basic requirements:

- it is necessary to use Li_2O as a precipitator in an amount exceeding stoichiometric;
- the use of oxygen for the deposition of rare-earth metals and uranium is impractical;

In order to experimentally justify the filtering process of the chloride melts containing the REE oxides, the tests were performed using the cerium oxide obtained by the oxidation of the cerium metal (brand CeE-0 (TC 48–4– 529.90)) in air.

The filtration rate, using the Al_2O_3 filters with a working porosity of 39% (figure 8), decreased from 45 to 40 cm^3 / hour • cm^2, depending on the volume of the chloride melt passed through the filter from 10 to 70 ml, respectively. The granulometric composition of the filtered Ce_2O_3 powder did not change, which indicates the high efficiency of the filtration process (figure 9).

The tested oxide aluminum filters can be recommended as filtering materials for melts based on alkali chlorides. For further practical use of the ceramic filters, it is necessary to work out the methods for interfacing these products with the structural materials of the proposed filtration process instrumentation. Furthermore, the metal filters made of nickel and stainless steel are currently being tested.

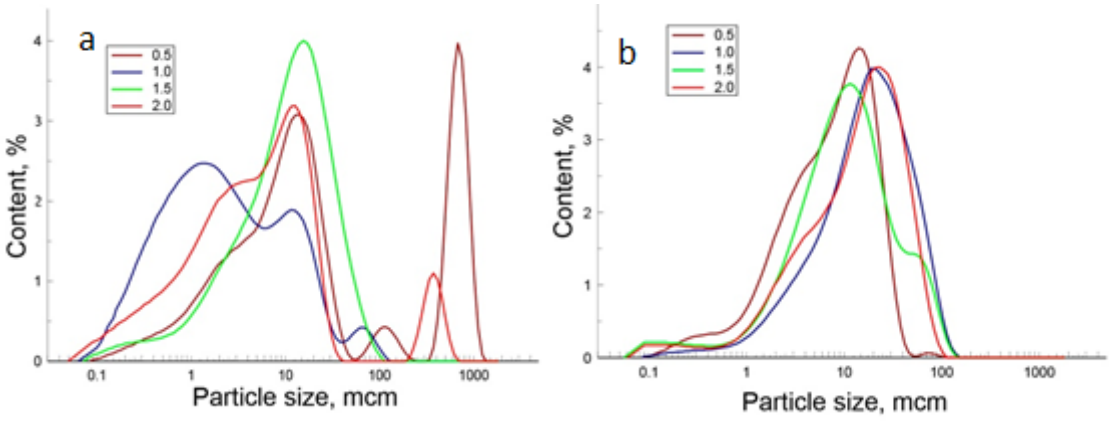

Figure 7. Differential curves of the particle size distribution for deposits obtained by the interaction of lithium oxide with the (3LiCl – 2KCl) –NdCl3 melt at different temperatures, ° C: 550(a); 750(b). The initial molar ratio O2–: Nd3 + are given in the graphs for each data set.

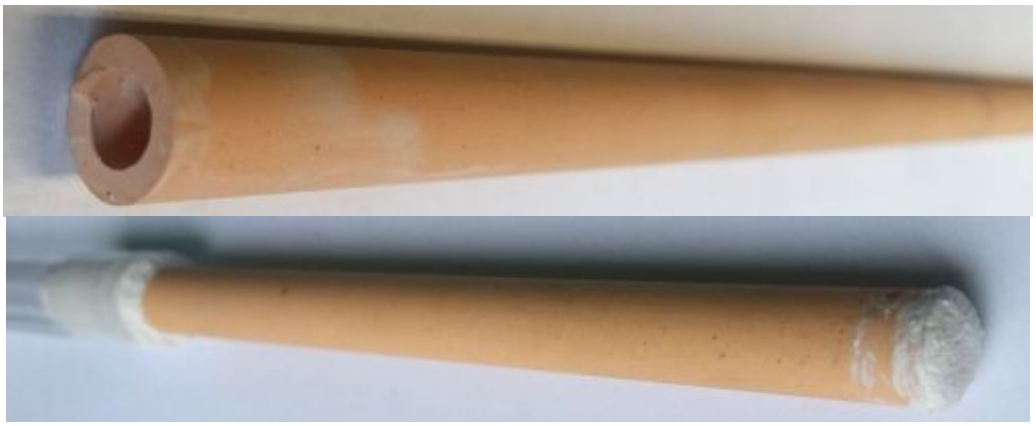

Figure 8. The layout of the aluminum oxide filter element (top) and filter assembly (bottom).

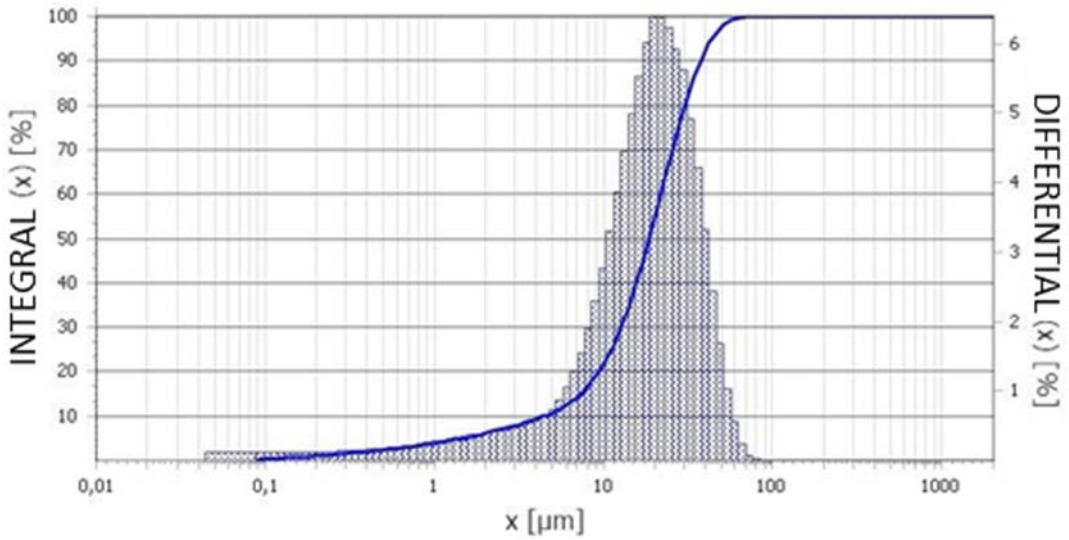

Figure 9. Granulometric composition of cerium oxide powder, filtered using the Al2O3 filter in the 3LiCl – 2KCl melt.

4.6. Regeneration of chloride electrolyte (purifying from alkaline and alkaline-earth FP)

The characteristics of the electrolyte purification process (LiCl, LiCl-KCl) from the CsCl and $SrCl_2$ impurities are determined by means of the zone recrystallization. In all experiments the obtained salt ingot can be divided into two sections: in the first (long) section, there is a decrease in the impurity concentration in comparison with its initial amount, and in the second (short), there is a significant enrichment in the CsCl and $SrCl_2$.

The purification degree of the chloride melt from the CsCl and SrCl2 depended on the composition of the salt-solvent, the initial impurity concentration, and the rate of the recrystallization front. In the purification process of the LiCl containing CsCl and $SrCl_2$ in an amount of 0.3 mol. %, the content of impurities was reduced by 10 times, and the volume of the purified salt was 80% of the total salt used in the experiment.

With increasing the CsCl and $SrCl_2$ concentrations to 3 mol. % in order to achieve a required degree of purification (a tenfold decrease in the impurities concentration) the amount of pure salt should be reduced to 60%. When the LiCl is replaced by the 3LiCl-2KCl eutectic mixture, the nature of the impurities distribution along the ingot length is retained; however, in order to obtain comparable results the recrystallization rate should be reduced by 6-10 times, and the length ratio of the “boat” to its width should be increased. The local increase in the impurities concentration to the values corresponding to the eutectic compositions leads to a decrease in the melting temperature and an increase in the width of the molten zone.

5. Conclusions

The results of the experimental research with the use of uranium, obtained in 2016–2017, confirmed the fundamental feasibility of the implementing the basic technological procedures of the pyrochemical SNF processing, that is the “soft” UN chlorination, reduction of the uranium dioxide during the electrolysis of the molten LiCl-Li2O (“metallization”), electrolytic deposition of the uranium metal in the chloride melt, and the oxide deposition of the rare earth elements.

Promising results related to the application of the distillation method in order to purify the products of metallization and the cathode deposits of uranium from the electrolyte, the filtering process of chloride melts containing REM oxides (on example of the cerium oxide), and the chloride electrolyte purification from the alkali and alkali-earth FP using zone recrystallization were obtained.

Further research will be focused on studying the behavior of other NM imitators (Pu, Am) and FP (Zr, Mo, noble FP) during the pyrochemical processing of the SNF FNR.

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